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An integrated model for assessing the risk of TCE groundwater contamination to human receptors and surface water ecosystems

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Abstract

The practical implementation of the European Water Framework Directive has resulted in an increased focus on the hyporheic zone. In this paper, an integrated model was developed for evaluating the impact of point sources in groundwater on human health and surface water ecosystems. This was accomplished by coupling the system dynamics-based decision support system *CARO-PLUS* to the aquatic ecosystem model *AQUATOX* using an analytical volatilization model for the stream. The model was applied to a case study where a TCE contaminated groundwater plume is discharging to a stream. The TCE source will not be depleted for many decades, however measured and predicted TCE concentrations in surface water were found to be below human health risk management targets. Volatilization rapidly attenuates TCE concentrations in surface water. Thus, only a 300 m stream reach fails to meet surface water quality criteria. An ecological risk assessment found that the TCE contamination did not impact the stream ecosystem. Uncertainty assessment revealed

hydraulic conductivity to be the most important site-specific parameter. These results indicate that contaminant plumes with μgL^{-1} concentrations of TCE entering surface water systems may not pose a significant risk.

Key words system dynamics; risk-based approaches; integrated modeling; chlorinated solvents; uncertainty; hyporheic zone; contaminated sites

1. Introduction

The practical implementation of the European Water Framework Directive (WFD) has generated many new challenges for water managers across Europe. As global exploitation of both stream water and groundwater increases, it is becoming more evident that managers need to develop an awareness of the linkages between these two systems, the roles that these linkages play in maintaining water quality, and how human activities may impair them (Hancock, 2002). In recognition of this, implementation of the WFD within the individual countries necessitates the evaluation of all types of contamination sources (e.g. point and diffuse) within a specific watershed in order to assess their direct impact on water quality and ecosystem health. It is required that surface water must meet good water quality and minimum ecological criteria, and that groundwater must have good chemical status.

Chlorinated solvents, such as trichloroethylene (TCE), and pesticides are among the most prevalent and serious contaminants of surface and groundwater resources in the world (e.g. Winter et al., 1998, Stroo et al., 2003; Guilbeault et al., 2005). In Denmark this is a major problem because almost all drinking water comes directly from groundwater (Henriksen et al., 2008). And many of these compounds are either acknowledged or suspected carcinogens (U.S. EPA, 2009b). Due to their widespread use, mobility and persistence, chlorinated volatile organic compounds (VOCs) are considered to have the greatest potential to discharge to surface waters (Ellis and Rivett, 2007).

Water management decisions are increasingly being based on model studies (Scholten et al., 2007) and modeling tools are becoming progressively more sophisticated, i.e. parameterized. Existing risk-based studies of coupled groundwater-surface water systems have tended to focus explicitly on predicting diffuse source transfers to surface waters (Heathwaite et al., 2005; Kannan et al., 2007). The use of these models, however, implies access to enough good quality data in order to both calibrate and validate the physical system before these models can be used in a predictive capacity. Simpler modeling approaches and tools also exist, but here the focus has typically been on either the groundwater (e.g. Troldborg et al., 2008) or the surface water system (e.g. Ani et al., 2009). Risk-based approaches capable of predicting and quantifying the impacts of groundwater contamination on surface water resources and ecosystem health are currently unavailable.

This paper aimed to bridge this gap by presenting a novel risk-based, source-pathway-receptor methodology for analyzing point source impacts to both human and ecological receptors, especially for use at early decision levels. Uncertainty assessments must be incorporated into the decision-making process, with emphasis throughout the modeling process (Refsgaard et al., 2007). Thus, the proposed approach also endeavors to produce "usable" scientific information by specifically addressing the role uncertainty plays on the decision-making process, particularly with respect to the use of "effective" parameters in groundwater transport modeling.

In this paper, we show how integrated modeling can support both human health and ecological risk assessments for evaluating surface waters impacted by point sources in groundwater. This is accomplished by coupling the system dynamics-based decision support system *CARO-PLUS* to the process-based aquatic ecosystem model *AQUATOX* through a simple analytical volatilization model. The system dynamics approach implemented in *CARO-PLUS* (Serapiglia et al., 2005; McKnight and Finkel, 2008) is particularly suited for management issues regarding contaminated land since it has the ability to incorporate past

actions (e.g. previous remedial strategies) that may have been undertaken to alleviate a problem (e.g. groundwater contamination). *AQUATOX* (Park et al., 2008) was found to be the most comprehensive of the few existing general ecological risk models, capable of representing the combined environmental fate and effects of toxic chemicals and their impacts to aquatic ecosystems.

2. Case study site – Skensved stream

A TCE contaminant plume that is leaching from groundwater into Skensved stream in Denmark is assessed with the new system dynamics tool. The Skensved stream, located on the eastern side of the island of Sjaelland in Denmark, has a catchment area of 25 km^2. Lille Skensved is located in an area with protected drinking water interests. Lille Skensved Waterworks is situated approximately 1.5 km northwest of the town. A second well field, for Lyngen Waterworks (Christensen and Raun, 2005), lies 3 km east of Lille Skensved and immediately south of the Skensved stream.

The aquifer at Skensved is contaminated by TCE originating from an auto lacquer shop in Lille Skensved which has used the solvent for degreasing metal parts since 1974. A leaking storage tank was found in 1993 where TCE had been seeping directly into the ground below. In 2003 it was determined that this storage tank was solely responsible for the TCE contamination in the aquifer, with a plume extending up to 1,000 m from the source area (see Figure 1, Christensen and Raun, 2005).

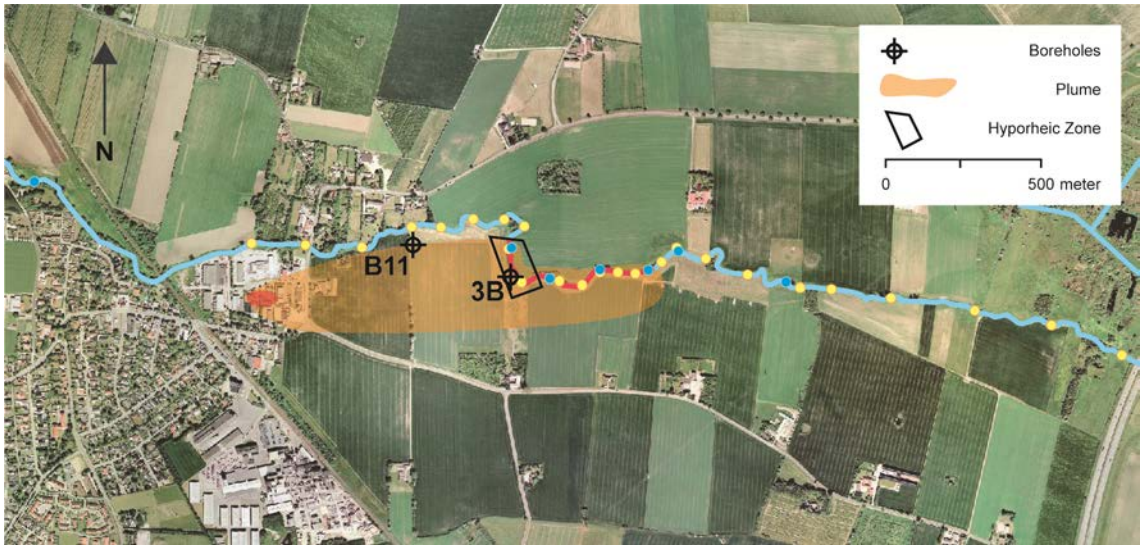

Figure 1: Propagation of the TCE contaminant plume and impacted stream section at the Lille Skensved site. Also shown are the measurement locations in the stream (yellow dots) and stream bed (blue dots), the location of the remediation well (B11) used for pump and treat, and the location of the well in the hyporheic zone (3B).

The geology beneath Lille Skensved and Skensved stream consists of 2-4 m of alternating layers of soil, gravel, sand and clay followed by 8–10 m of bryozoan limestone (the Danien Limestone) that is underlain by a low permeability zone (GEO, 2009). The primary limestone aquifer is characterized by an effective hydraulic conductivity of 19 md^{-1}, a hydraulic gradient of 0.00473 (Christensen and Raun, 2005), and an effective porosity of 0.02 (GEO, 2009), resulting in seepage velocities on the order of 4.5 md^{-1}. Since no information is available on the mass fraction of organic carbon, a typical literature value of 0.002 for Danish aquifer materials was assumed (corresponding to a retardation value of 44 for TCE, Christensen et al., 1996).

Although little data exist regarding the specific source zone characteristics (e.g. geometry), measured TCE concentrations (in the mgL^{-1} range) in the primary aquifer below the source indicate the presence of separate phases of chlorinated solvents (Christensen and Raun, 2005). GEO (2009) estimates that 150–240 tons of TCE have been used in the auto

lacquer shop during the period from 1974 to 1999. Furthermore, GEO (2009) conclude that the TCE plume is under hydraulic control through the implementation of pump and treat. Approximately 60,000 to 100,000 m^3yr^{-1} of water have been pumped from the source area, as well as 30,000 to 100,000 m^3yr^{-1} from well B11 (indicated on Figure 1, Christensen and Raun, 2005; GEO, 2009). Current plans are to continue with the pump and treat strategy until 2010 (GEO, 2009).

The average water flux in the Skensved stream was determined to be 13,500 m^3d^{-1} (157 Ls^{-1}), based on data taken over the past 20 years, with large interannual and seasonal variation (Christensen and Raun, 2005). In 2005, the water flow decreased from 1,200 Ls^{-1} in early January to just 6.3 Ls^{-1} in July and August (data not shown, Bruun and Rose, 2005). The changing water flow directly affects the water levels in the stream so that, in 2005, the water depth rose to more than 50 cm during the winter months and dropped below 20 cm in the summer. In late September of 2005, water levels as low as 11 cm were observed.

In previous studies, conducted through the Technical University of Denmark in 2005 and 2008, the extent of groundwater-surface water interaction at the site has been determined using piezometers and temperature measurements. Danish groundwater usually has a temperature of 10ºC, and so a local surface water temperature rise occurs in the winter when groundwater enters the stream, as the surface water is colder than the groundwater. The reverse occurs in the summer. The measurements, taken along 4 km of the stream (indicated by yellow dots in Figure 1), clearly show a temperature change in the hyporheic zone indicating that groundwater influx to the stream occurs (data not shown).

Further evidence of groundwater-surface water interaction is obtained through groundwater monitoring data. The data show that the TCE concentration in groundwater declines from the west to east side of the stream, as illustrated in Figure 2, indicating that a significant fraction of TCE (maximum concentration of 120 μgL^{-1} in borehole 3B) is entering the Skensved stream. Seepage meter samplers placed in the hyporheic zone show that concentrations of up

to 59 μgL^{-1} occur in groundwater entering the stream. The infiltration rates at three different locations along the stream were determined: 336 $Lm^{-2}d^{-1}$ at 1,674 m, 84 $Lm^{-2}d^{-1}$ at 1,765 m and 170 $Lm^{-2}d^{-1}$ at 1,943 m (compare distances with Figure 6). Based on these seepage meter measurements, the flux of contaminants from groundwater into the stream could be determined.

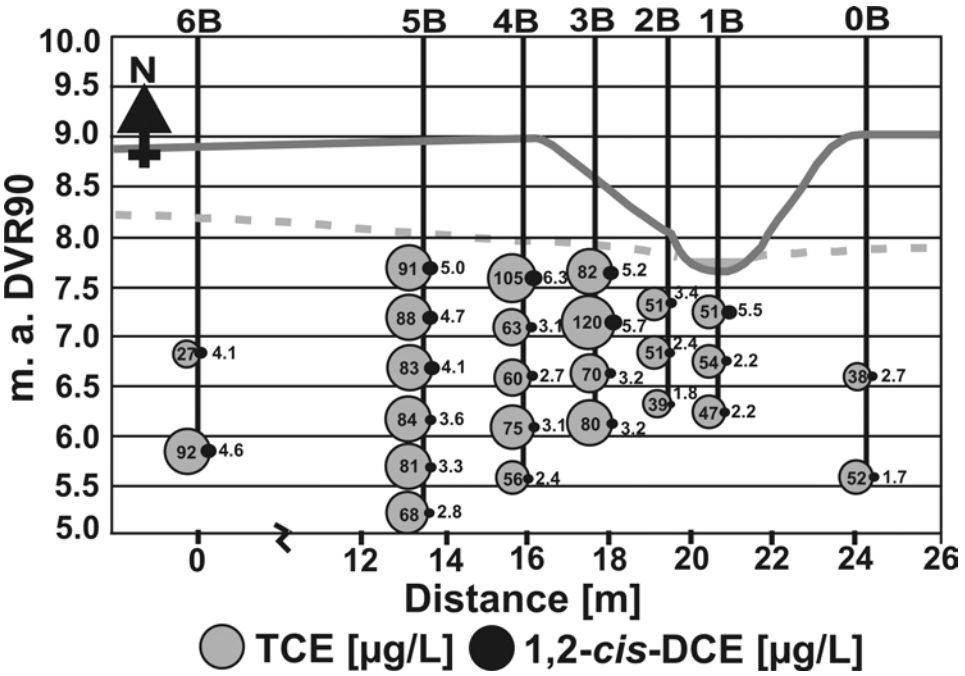

Figure 2: TCE and 1,2-*cis*-DCE concentrations [μgL^{-1}] in the groundwater moving west to east (left to right) from the source zone to the east bank of the Skensved stream (Christensen and Raun, 2005). Well 3B was found to contain the highest TCE concentrations, which was used for calibrating the source release model.

In the surface water in August 2005, the TCE concentration increased from zero to a maximum of 17.4 μgL^{-1} along a 250 m stretch where the groundwater plume interacts with the Skensved stream, and decreased thereafter to zero again. Thus, it was concluded that the contaminant plume enters the stream between 1,625 m and 1,875 m. TCE was also observed in the stream on other occasions, but annual maximums occurred during the summer months.

The bottom sediments are generally highly permeable and contain insignificant amounts of organic matter. Water chemistry and redox parameters were measured in May–June 2005 using both multilevel samplers and seepage meters for the influent groundwater, as well as directly from the surface water (Table 1). Based on these results, the hyporheic zone could be characterized as being slightly aerobic and/or nitrate-reducing, thus preventing significant anaerobic dechlorination (Scheutz et al, 2008; Abe et al., 2009). No apparent increase in 1,2-*cis*-DCE was observed in the groundwater to the west of the stream (Figures 1 and 2), or in the stream itself. And so it was concluded that no overall systematic degradation of TCE is taking place in the down-gradient portion of the plume.

TABLE 1

3. Methodology: integrated modeling framework

The impacts of TCE on Skensved stream was assessed using a source-pathway-receptor concept (see Figure 3). The conceptual model was implemented by coupling the system dynamics model *CARO-PLUS* to the U.S. EPA ecological impact assessment model *AQUATOX*. This was necessary since *CARO-PLUS* is currently equipped only for the analysis of risks to human health, specifically when the contamination plume at the receptor occurs in groundwater (note however that the source zone can originate either in soil, groundwater or both). Similarly, the U.S. EPA model *AQUATOX* is equipped only for the analysis of ecological effects on aquatic ecosystems when the contaminants are already present in the surface water.

In order to enable both a quantitative human health risk assessment and an ecological risk assessment of this site, the decision support system *CARO-PLUS* was coupled to the process-based aquatic ecosystem model *AQUATOX* through a simple analytical surface water

volatilization model. The model was constructed in order to track the fate of TCE as it moves from the groundwater through the groundwater-surface water interaction zone (i.e. hyporheic zone) into surface water. These steps will be described in more detail in the following sections.

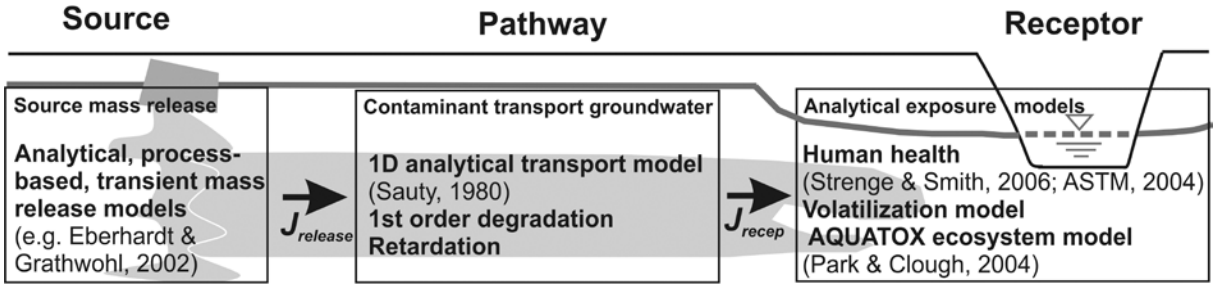

Figure 3**: Schematic illustration of the source-pathway-receptor concept implemented in the program** *CARO-PLUS***.**

3.1 System dynamics modeling: *CARO-PLUS*

CARO-PLUS, developed at the Center for Applied Geoscience/University of Tuebingen, is intended to be used for preliminary assessment as part of a tiered approach, and to allow the user to simulate and optimize the effects of potential remedial actions including tackling the contaminant source and managing groundwater plumes (McKnight, 2009). It currently consists of a source release module, a contaminant transport module and a human health impact assessment module. Both mass release and contaminant transport in groundwater are quantified using transient models that are based on analytical approaches (Sauty, 1980; Huntley and Beckett, 2002; Eberhardt and Grathwohl, 2002; Peter et al., 2008). The existing contamination and its further development can be evaluated on the basis of contaminant mass fluxes, concentrations, and risk indices (carcinogenic/non-carcinogenic). Possible remedial actions causing mass flux changes over time are also simulated (McKnight, 2009).

CARO-PLUS also contains a risk assessment module that describes exposure pathways, i.e. transport (transfer) of contaminants from groundwater to the receptor “human being”, in accordance to the Multimedia Environmental Pollutant Assessment System developed by Strenge and Smith (2006). The model is capable of analyzing pollutant behavior in various media (air, soil, groundwater and surface water) and estimating transport through and between media. The uncertainty inherent in both site-specific and exposure parameters is explicitly taken into account using Monte-Carlo simulations.

CARO-PLUS is built on the system dynamics platform Vensim (Ventana Systems, 2007). System dynamics uses an interlinked system of stocks (levels) and flows (rates). Water, as well as contaminant mass can be thought of and measured using stock terms, which describe the volume or mass present at a particular place and point in time. Similarly, water and mass transfer can be calculated using flow terms, which describe the volume or mass reaching or passing a defined point or area in a given time period. The overall structure of the model as implemented in a systems dynamics framework is described in Figure 4. The stocks are represented in the figure using boxes and the flows by double arrows. The single arrow terms show the most important inputs required in calculations. The model has been tested for appropriateness and verified in McKnight (2009).

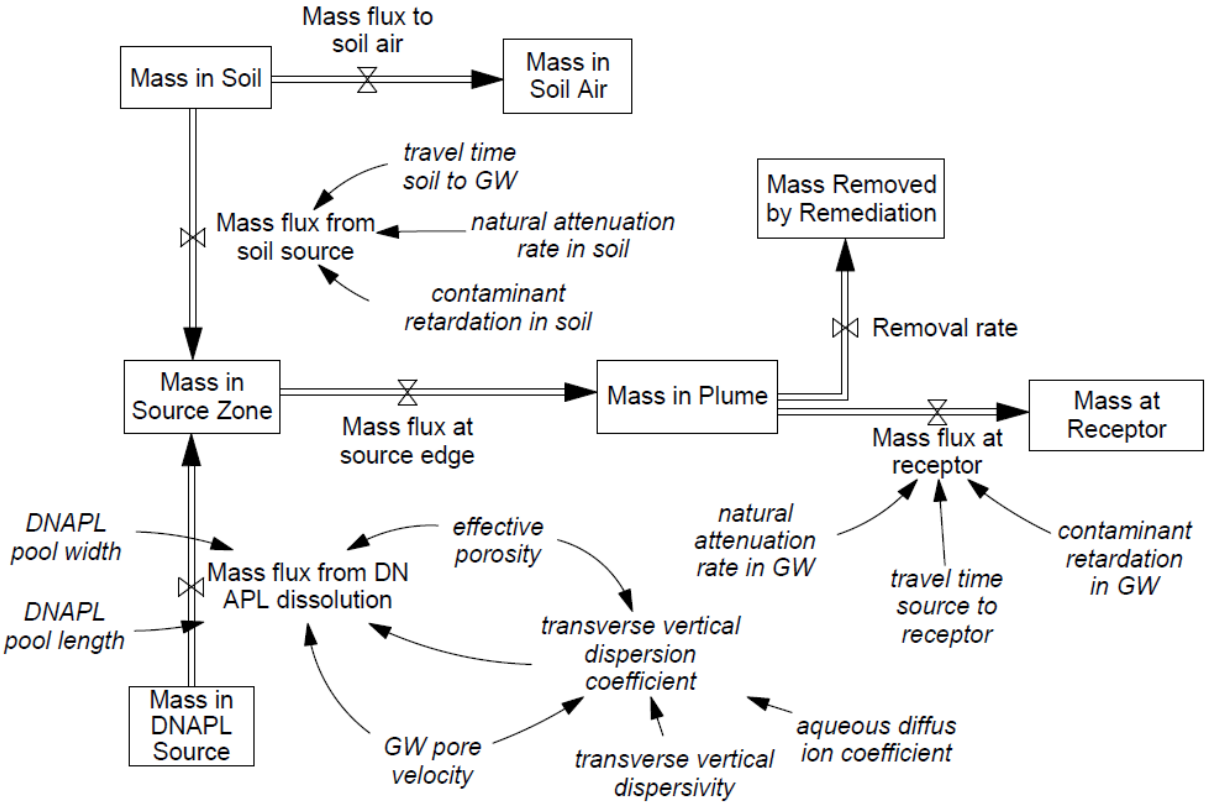

Figure 4: Major structure for the DNAPL pool release scenario and transport along the groundwater pathway, including retardation and degradation.

3.1.1 Source characterization: contaminant emission from DNAPL pool

The source model conceptually distinguishes between light and dense NAPL contamination scenarios, as well as residual phase or blob zones. The organic contaminant phase is typically described as a mixture of multiple compounds, but single compound scenarios can also be modeled. Mass release from a DNAPL pool is quantified using a model which describes the dispersive mass transfer of DNAPL into groundwater flowing across the pool, with the resultant flux being given by (Eberhardt and Grathwohl, 2002):

$$J_i^{dnapl} = C_{w,i}^{sat} B_p L_p n_e \sqrt{\frac{4Dv_x}{\pi L_p}} \qquad (1)$$

where J_i^{dnapl} [MT^{-1}] is the dissolution rate of compound *i* from a pool with width B_p [L] and length L_p [L], and D [L^{2}T^{-1}] is the transverse vertical hydrodynamic dispersion coefficient, which is calculated using:

$$D = D_p + \alpha_{tv} v_x \quad (2)$$

where D_p [L^{2}T^{-1}] is the pore diffusion coefficient (also approximated as $D_{aq} n_e$) and α_{tv} [L] the transverse vertical dispersivity.

The values for transverse vertical dispersivity are estimated by assuming that dispersion can be represented as a linear function of groundwater pore velocity (Klenk and Grathwohl, 2002). Other assumptions inherent to this solution include constant concentration at the NAPL-water interface where dissolution occurs, and equilibrium is assumed to have been reached between the NAPL and a boundary layer of water (i.e. bordering the DNAPL pool).

3.1.2 Groundwater contaminant transport

The mass transfer of the contaminant from the source to the stream is modeled analytically, assuming steady-state (averaged) flow conditions, advective and diffusive transport, retardation and biodegradation (i.e. when applicable) by (Sauty, 1980):

$$J_R = \frac{J_{SE}}{2} erfc\left(\frac{L_x - v_{x,R} t_R}{2\sqrt{\alpha_L v_{x,R} t_R}} \right) e^{-\frac{\lambda_i L_x}{v_x}} \quad (3)$$

where J_R [MT^{-1}] is the estimated mass flux at the receptor, J_{SE} [MT^{-1}] is the mass flux at the down-gradient edge of the source, L_x [L] is the distance between the source and the receptor in the *x*-direction, α_L [L] is the longitudinal dispersivity, t_R [T] is the simulation time, λ_i [T^{-1}] is the first-order biodegradation rate for compound *i*, and v_x [LT^{-1}] is the groundwater pore velocity. The parameter values employed are the average (or effective) values for the pathway between the source and receptor. The longitudinal dispersivity is directly estimated in *CARO-PLUS* by (Xu and Eckstein, 1995):

$$\alpha_L = 0.83\,[\log(L_x)]^{2.414} \quad (4)$$

3.2 Analytical volatilization model

A stream transport model is developed to describe the transfer of mass into the stream from groundwater and the subsequent volatilization of contaminant from the stream. The model is based on the observation that volatilization is likely to be the dominant process affecting the concentration of VOCs in stream water (Rathbun, 2000).

The model considers a stream of constant volume, where inflow equals the outflow. The change in concentration of a VOC over time for a given volume of water is given by:

$$V\frac{dC(t)}{dt} = Q_{gw}C_{gw} - K_v C(t)V \quad (5)$$

where V [L^3] is the volume of the water body, Q_{gw} [L^3T^{-1}] and C_{gw} [ML^{-3}] are the flux and VOC concentration of the infiltrating groundwater, respectively, K_v [T^{-1}] is the volatilization rate and $C(t)$ [ML^{-3}] is the VOC concentration at time t [T]. If the initial VOC concentration is $C(0) = 0$, then the solution of (5) is given by:

$$C(t) = \frac{C_{gw}Q_{gw}}{K_v V} - \frac{e^{-K_v t}C_{gw}Q_{gw}}{K_v V} \quad (6)$$

When the initial VOC concentration is not zero, the solution becomes:

$$C(t) = \frac{C_{gw}Q_{gw}}{K_v V} + e^{-K_v t}\left(C_{t-1} - \frac{C_{gw}Q_{gw}}{K_v V}\right) \quad (7)$$

where C_{t-1} [ML^{-1}] is the initial VOC concentration. Equation (7) can be used for scenarios where the infiltration rates Q_{gw} and/or the VOC groundwater concentrations C_{gw} are not constant over the distance of the modeled stream.

3.3 Risk assessment

3.3.1 Human health risk assessment

The risk to human health due to direct or indirect exposure to contaminated water (e.g. ingestion of water or leafy vegetables) can be assessed using a methodology that is applicable to both groundwater and surface water. In *CARO-PLUS*, the risk assessment is focused on the risks associated with pollutants originating in groundwater. Here the human health risk assessment was extended to also consider surface water contaminants. The risk assessment begins with identified concentrations of the constituents of interest which are then converted to average daily doses at the point of exposure (e.g. receptor location in Figure 3). The doses are then converted to risk values for either carcinogens (evaluated as total risk level, $RL_{tot,i}$ [-]) or non-carcinogens (total hazard quotient, $HQ_{tot,i}$ [-]) using:

$$RL_{tot,i} = \sum_{k=1}^{n_E} LADD_i * SF_i$$
$$HQ_{tot,i} = \sum_{k=1}^{n_E} \frac{CADD_i}{RfD_i} \quad (8)$$

where $LADD_i$ [$MM^{-1}T^{-1}$] is the lifetime (cancer) average daily dose, SF_i [$MM^{-1}T^{-1}$]$^{-1}$ is the corresponding (oral) slope factor, k is the exposure pathway, i is the pollutant, n_E [-] is the number of exposure pathways considered, $CADD_i$ [$MM^{-1}T^{-1}$] is the chronic average daily dose and RfD_i [$MM^{-1}T^{-1}$] is the corresponding (oral) reference dose.

The risk values ($HQ_{tot,i}$; $RL_{tot,i}$) are then summed over all the (known) compounds considered for a particular site in order to produce a risk (or hazard) index:

$$RI = \sum_{i=1}^{n_C} RL_{tot,i}$$
$$HI = \sum_{i=1}^{n_C} HQ_{tot,i} \quad (9)$$

where RI [-] is the risk index, n_C [-] is the number of compounds considered and HI [-] is the hazard index. Major assumptions include that exposure to any amount of a carcinogen will increase the cancer risk (i.e. no threshold dosage), risks are additive for multiple chemicals and (exposure) routes, and potential synergistic effects (between compounds) are not considered.

$LADD_i$ and $CADD_i$ result from exposure pathway functions (Strenge and Smith, 2006) that are based on a specific set of parameters (see equation 10). These parameters are typically set to default values considered to be standard for a particular risk group (e.g. children) and toxicity assessment (e.g. carcinogens). The toxicity assessment is conducted using existing databases such as the Integrated Risk Information System (IRIS), maintained by the U.S. Environmental Protection Agency (U.S. EPA, 2009b), and the Risk Assessment Information System (RAIS) that is maintained by Oak Ridge National Laboratory for the U.S. Department of Energy (RAIS, 2009). The goal is to provide an estimate of the relationship between the magnitude of exposure and severity (non-carcinogens) or likelihood (carcinogens) of adverse effects. Thus, for carcinogens and for each exposure pathway, $LADD_i$ can be determined by a set of equations following the U.S. EPA (1991; 2001; 2004) and ASTM (2004):

$$LADD_{i,ing} = C_{i,w}\left[IR_w \frac{EF * ED}{BW * AT * 365\frac{d}{yr}}\right]$$

$$LADD_{i,inh} = C_{i,a}\left[IR_a \frac{EF * ED}{BW * AT * 365\frac{d}{yr}}\right]K \qquad (10)$$

$$LADD_{i,dc} = C_{i,w}\left[SA * ET \frac{EF * ED}{BW * AT * 365\frac{d}{yr}}\right]K_p * CF_1$$

where $LADD_{i,ing}$, $LADD_{i,inh}$ and $LADD_{i,dc}$ are the average daily doses for the ingestion, inhalation and dermal contact pathways, respectively, $C_{i,w}$ [mgL^{-1}] and $C_{i,a}$ [mgm^{-3}] are the concentrations in water and air, respectively, IR_w [Ld^{-1}] is the water ingestion rate, IR_a [m^3d^{-1}] is the inhalation rate, SA [m^2] is the exposed skin surface, ET [hrd^{-1}] is the exposure time for an outdoor activity, EF [dyr^{-1}] is the frequency of exposure to the contaminant, ED [yr] the exposure duration, BW [kg] is the bodyweight, AT [yr] is the period over which the time is averaged, K [Lm^{-3}] is the Andelman volatilization factor for chemical pollutants, K_p [$cmhr^{-1}$]

is the skin permeability coefficient for chemical *i* and CF_1 [$Lmcm^{-1}m^{-3}$] is a unit conversion factor.

3.3.2 Ecological risk assessment

This paper extends the *CARO-PLUS* model to assess the ecological impact of contaminants in surface water. An ecological risk assessment can be carried out in several ways. A rudimentary (i.e. conservative, screening level) method is to compare exposure point concentrations with ecotoxicity values for a set of ecological receptors using (U.S. EPA, 1997a):

$$HQ_i = \frac{EEC_i}{NOAEC_i} \tag{11}$$

where HQ_i [-] is the hazard quotient for pollutant *i*, EEC_i [ML^3] is the estimated concentration at the exposure point and $NOAEC_i$ [ML^3] is the no-observed-adverse-effects-concentration. The $NOAEC_i$ values were taken from the online database ECOTOX maintained by the U.S. EPA (2009a). The U.S. EPA advises that these conservative results can be used to determine whether ecological threats are negligible or whether a more detailed ecological risk assessment is required.

The simple ecological assessment approach described above has been criticized since $NOAEC_i$ reference values exist only for a few ecological receptors and a high uncertainty exists for the extrapolation of these values to other organisms (Tannenbaum, 2005). A more comprehensive ecological risk assessment can be made using the freshwater ecosystem simulation model *AQUATOX*. *AQUATOX* combines the simulation of an aquatic ecosystem with the environmental fate and effect of various pollutants, such as nutrients and organic chemicals. The model is capable of computing endpoint concentrations for pollutants in both water and bottom sediments, as well as their effects on a variety of aquatic flora and fauna. A

detailed description of *AQUATOX* including the specific calculations for ecosystem health parameters is included in Park and Clough (2004), Park et al. (2008) and references therein.

3.4 Uncertainty assessment

One of the goals of this paper is to carry out a quantitative exposure assessment, including an in-depth investigation into how uncertainty influences management decisions. By segregating the uncertainties that are specific for the exposure parameters in a particular land use scenario from those that are site- and contaminant-specific, the investigator can work to reduce the uncertainties associated with the site, while being able to recognize the uncertainties inherent in the exposure process. This process leads to robust management strategies.

Uncertainty was investigated using Monte-Carlo simulation of the site-specific parameters within *CARO-PLUS*. A Latin hypercube method was used to sample parameter values from given distributions. After generation of the Monte-Carlo output, the simulation results were post-processed to remove model outcomes that lie outside a predefined acceptable range. This “model screening” is a necessary measure since parameter values inherent to the Monte-Carlo process are drawn randomly from their individual probability distributions, and can therefore be combined in ways that are physically infeasible and their consideration would decrease the validity of the results.

4. Results: application to Skensved stream

4.1 Source characterization and groundwater transport model

The *CARO-PLUS* model was utilized to simulate the TCE flux from the source area to the hyporheic zone as a function of time. Table 2 presents a summary of the general parameter values implemented in the base case scenario. Hydraulic conductivity was used as a calibration parameter for (model) transport, based on the range given in Christensen and Raun

(2005). All further transport parameters could be taken either from site-specific investigations or the literature.

The historical conditions in the source zone are not known, and so observed concentrations measured down-gradient of the source zone for two different points in time (1995 – pre-pump and treat – and 2005) are used to calibrate the source zone geometry in the model (see results in Table 2). Measurement information for calibration of the transport model is taken from remediation well B11 (500 m down-gradient, Figure 1) and well 3B located in the hyporheic zone (750 m down-gradient, Figures 1 and 2). The model calibration assumes that TCE degradation is not occurring at this site, due to the prevailing redox conditions and absence of degradation products.

Calibration of the model results in an initial volume and mass of TCE of 33 m^3 and 48.2 tons, respectively. The calibrated model fits well to concentrations measured in 1995 of 280 μgL^{-1} at well B11 (compared with 309 μgL^{-1} modeled – data not shown) and 160 μgL^{-1} in well 3B (compared with 174 μgL^{-1} modeled, Figure 5b). A concentration of 120 μgL^{-1} was measured in well 3B in 2005 (see Figure 2), again comparing well with the modeled value of 129 μgL^{-1} (Figure 5b).

TABLE 2

4.2 Human health risk assessment based on groundwater concentrations

The results from the groundwater transport model can be used for an initial calculation of risk to human health. The cancer classification for TCE is still under review by the U.S. EPA (2009b). However, it is currently classified as a possible-probable carcinogen by the Agency for Toxic Substances and Disease Registry (ATSDR, 1997), and is listed as “medium priority” by the International Agency for Research on Cancer (IARC, 2008). Thus it makes sense to conduct the risk assessment for the case that TCE can be classified as carcinogenic.

In addition, the most sensitive target risk group is chosen – children. Table 3 lists the exposure pathways determined to be potentially relevant for this receptor. It should be noted that *CARO-PLUS* considers receptor endpoints such as surface water (i.e. fin fish ingestion, shoreline sediment ingestion) from a risk perspective. Contaminant concentrations in surface water are calculated by a simple dilution model, i.e. through mixing of the contaminated groundwater with surface water. The risk scenario was conducted for the worst-case, i.e. fish are assumed to ingest a mixture of groundwater and stream water where the amounts were determined by the groundwater flow rate and the low (summer) observed surface water flux.

Table 3 shows the results of the risk assessment: the exposure pathways considered and their associated maximum (calculated) risk index. The maximum concentration was calculated to be 247 μgL^{-1} in groundwater used for drinking (first occurring in July 2021) and the risk index was determined to be 5.68×10^{-4} (October 2021). These can be compared with target risk levels of 10^{-6} and maximum allowable TCE concentrations of 10 μgL^{-1} and 1 μgL^{-1} in surface and groundwater, respectively (Miljoe- og Energiministeriet, 1996; Miljoestyrelsen, 1998).

TABLE 3

Of the eight pathways considered for the receptor, only two pathways play a significant role in causing risk to the receptor (marked in bold in Table 3). The drinking water ingestion pathway assumes that groundwater is used directly for drinking water (e.g. from a private well) without treatment. The sum of the risk indices for the six least important pathways is 2.69×10^{-7}, thereby meeting the risk management target of 10^{-6}.

Figure 5 shows overall results of the risk assessment based on groundwater concentrations, including (a) mass depletion, (b) aqueous mass flux from NAPL source zone, (c) concentration at the receptor (750 m) and (d) risk index for a simulation period of 100

years. The figure shows the impact of the pump and treat (P&T) system used for source control and the outcome if pump and treat had not been employed. The effect of the pump and treat containment strategy can be seen in the decreasing concentrations and risk between 1999 and 2009. The model shows that if the current pump and treat system is switched off in 2009, then the concentration and risk will rebound in 2014. This means that, when the pump and treat action is terminated, both management targets of 1 μgL^{-1} in groundwater (Figure 5b) and RI = 10^{-6} (Figure 5d) will be exceeded in the base case scenario.

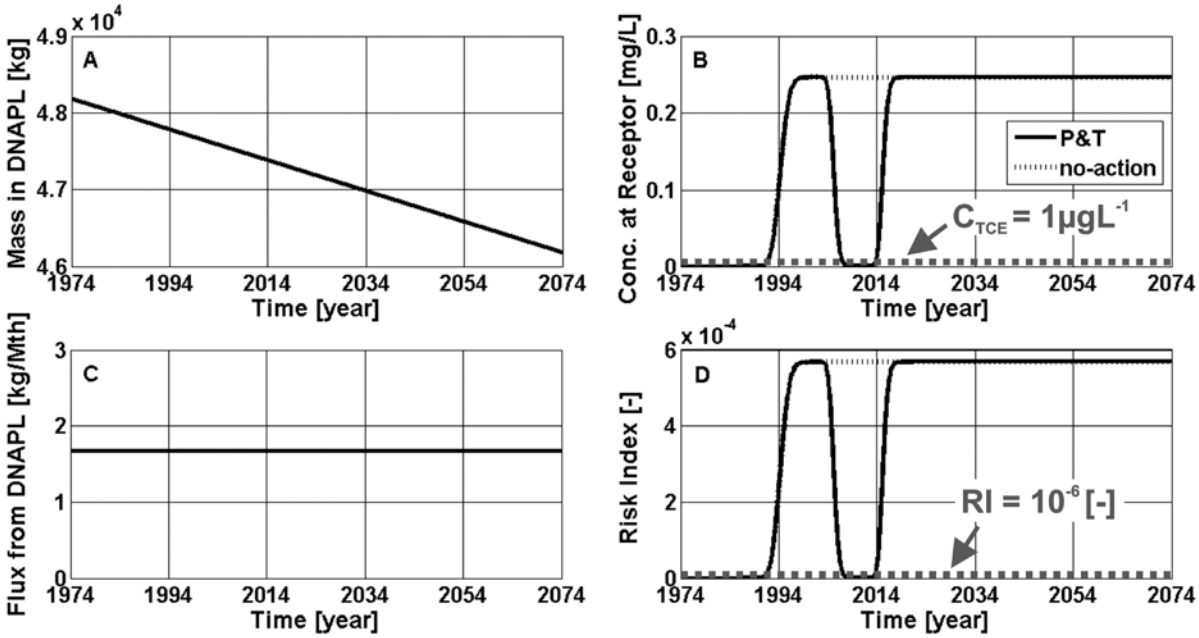

Figure 5: Output of the source zone and groundwater models: (a) mass depletion, (b) concentration at stream receptor (750 m), (c) aqueous mass flux from DNAPL source zone, and (d) risk index. Also shown, as a dashed horizontal line, are the management targets associated with (b) TCE concentration and (d) risk index.

4.3 Surface water transport model

The parameter values utilized in the analytical volatilization model are summarized in Table 4. Several of the parameters in the model are known to be nonstationary (e.g. surface water flow, cross-sectional area), in part due to seasonal changes. To evaluate the worst case,

the model was set up to simulate the conditions during the summer, which is characterized by low water fluxes and water levels.

TABLE 4

Using the volatilization and groundwater inflow rates as fitting parameters, the volatilization model was fitted to the measured TCE concentrations, as shown in Figure 6. Three separate groundwater inflow sections were identified, with the first occurring at 1625 m and approximately 250 m long, the second only 75 m long, and the third encompassing the remainder of the investigated stream section. The initial values for the first two groundwater inflow rates were taken from the measured data (e.g. 336 $Lm^{-2}d^{-1}$ at 1,674 m and 84 $Lm^{-2}d^{-1}$ at 1,765 m) and then adjusted. No initial data were available for the third rate. The figure shows two “jumps” in the TCE concentration at 2,125 m and 2,300 m and these can be explained by the model if it includes the increased groundwater infiltration rates at these points (see Figure 6).

The model can be used to determine the stream reach over which the surface water quality criteria for TCE has been exceeded, namely between 1,700 m and 2,000 m (Figure 6). That is, only 300 m of the Skensved stream is actually affected by the TCE contamination (i.e. fails to meet surface water quality criteria) from the contaminated groundwater.

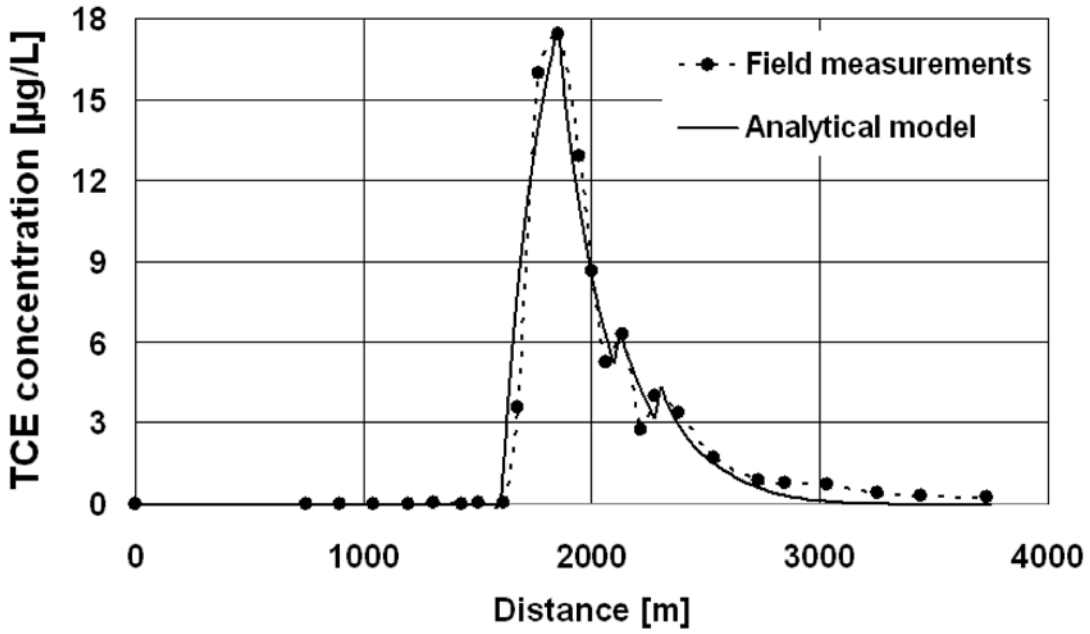

Figure 6: Analytical volatilization model (solid line) fitted to actual TCE concentrations (dashed line) measured in August 2005, by accounting for both volatilization and upstream inflows. The two "jumps" were fitted by including downstream groundwater-to-surface water influx areas.

4.4 Human health risk assessment based on surface water concentrations

The maximum modeled (and observed) TCE concentration in the surface water of 17.4 μgL^{-1} was used to assess the human health risk for children. This second human health risk assessment was conducted specifically for the potential exposure scenario of children playing outdoors in the contaminated stretch of Skensved stream. For a recreational land use scenario, risk from surface water is the sum of ingestion, inhalation and dermal contact with the water.

Isolating $LADD_i$ in equation 8 and then solving for the respective contaminant concentrations from equation 10 allows the determination of the maximum allowable concentrations in water and air for a specific risk target, e.g. $RI = 10^{-6}$. Using the parameter values listed in Table 5, the maximum allowable concentrations in water for the ingestion and dermal contact pathways were found to be 54.2 μgL^{-1} and 25.4 μgL^{-1}, respectively. Both of these values are above the TCE concentration actually measured in the stream. Similarly, the

maximum allowable concentration in air for the inhalation pathway was found to be 0.7 μgL^{-1}. No data exist for TCE concentrations in the air in this vicinity for comparison purposes.

TABLE 5

4.5 Preliminary ecological risk assessment in the stream

Indicator organisms were selected for the screening-level ecological risk assessment (e.g. according to equation 11), including *Daphnia magna* (aquatic crustaceans), mayfly and minnow (representing fin fish). TCE toxicity data can be found for these three organisms in the U.S. EPA ECOTOX database (U.S. EPA, 2009a). The respective hazard quotients were calculated to be 0.013, 0.0004 and 0.001, respectively, and all were well below the target value of 1. Neither *D. Magna* nor minnow are typically found in small Danish streams (Dall and Lindegaard, 1995). However, *D. magna* and minnow were chosen to represent *Gammarus pulex* (common freshwater shrimp) and (juvenile) *Salmo trutta* (brown trout), both of which are common inhabitants of small Danish streams (Dall and Lindegaard, 1995). Furthermore, species of the mayfly family, Baetidae, are frequently found in Danish streams. The chosen indicator organisms are thus assumed to represent different trophic levels in a simplified Danish stream ecosystem. NOAECs for *D. magna* and *G. pulex* are comparably low in terms of other toxicant groups (e.g. pesticides, Kronvang et al., 2003), and we therefore assume that *D. magna* here is representative of *G. pulex* as the most sensitive organism at the TCE polluted stretch in Skensved stream.

4.6 Comprehensive ecological risk assessment in the stream

In order to conduct a more comprehensive ecological risk assessment, the *AQUATOX* model was set up to model the 300 m stretch of the Skensved stream impacted by the TCE groundwater plume. Although the Skensved site was extensively characterized, much of the

data needed for input to *AQUATOX* were not available (e.g. lipid fraction for the various organisms modeled). Instead, unknown parameters were based on an existing case study in *AQUATOX*, where the impact of an organic toxicant is simulated and verified for a generic Ohio creek (see Table 6 for parameters). Biomasses of the included autotrophic components were maintained at low levels because of the small stream size and expected high level of human maintenance activities. Shading effects of stream bank vegetation increase proportionately with decreasing stream size (Allan, 1995). Furthermore, the vast majority of small Danish streams have lowered stream beds due to heavy and frequent maintenance which, additionally, increase shading effects of bank vegetation. We therefore propose that primary production is low at this impacted stretch of Skensved stream. Please note that some of the ecotoxicological parameters could be either estimated directly from the parameters given in Table 6 (e.g. animal/plant K2 elimination rate constants), or were estimated as suggested within the existing case study (e.g. animal EC50 growth/reproduction values were estimated using the *D. Magna* LC50/EC50 ratio; see U.S. EPA, 2009c for more details). The "Mannings Equation" method was selected for computing the water body volume in *AQUATOX*, based on existing (dynamic) outflow data for 2008.

TABLE 6

Figure 7a shows the observed stream discharge and modeled TCE concentration for one year. In July, the water volume reaches its annual minimum of 20 m^3 (over 300 m, corresponding to 0.8 m^3 per m stream), and the TCE concentration peaks at just over 16 μgL^{-1}. In general, the pattern of peaks seen on both curves shows that a clear correlation exists between the water volume and the TCE concentration, with high water volumes reflecting low TCE concentrations.

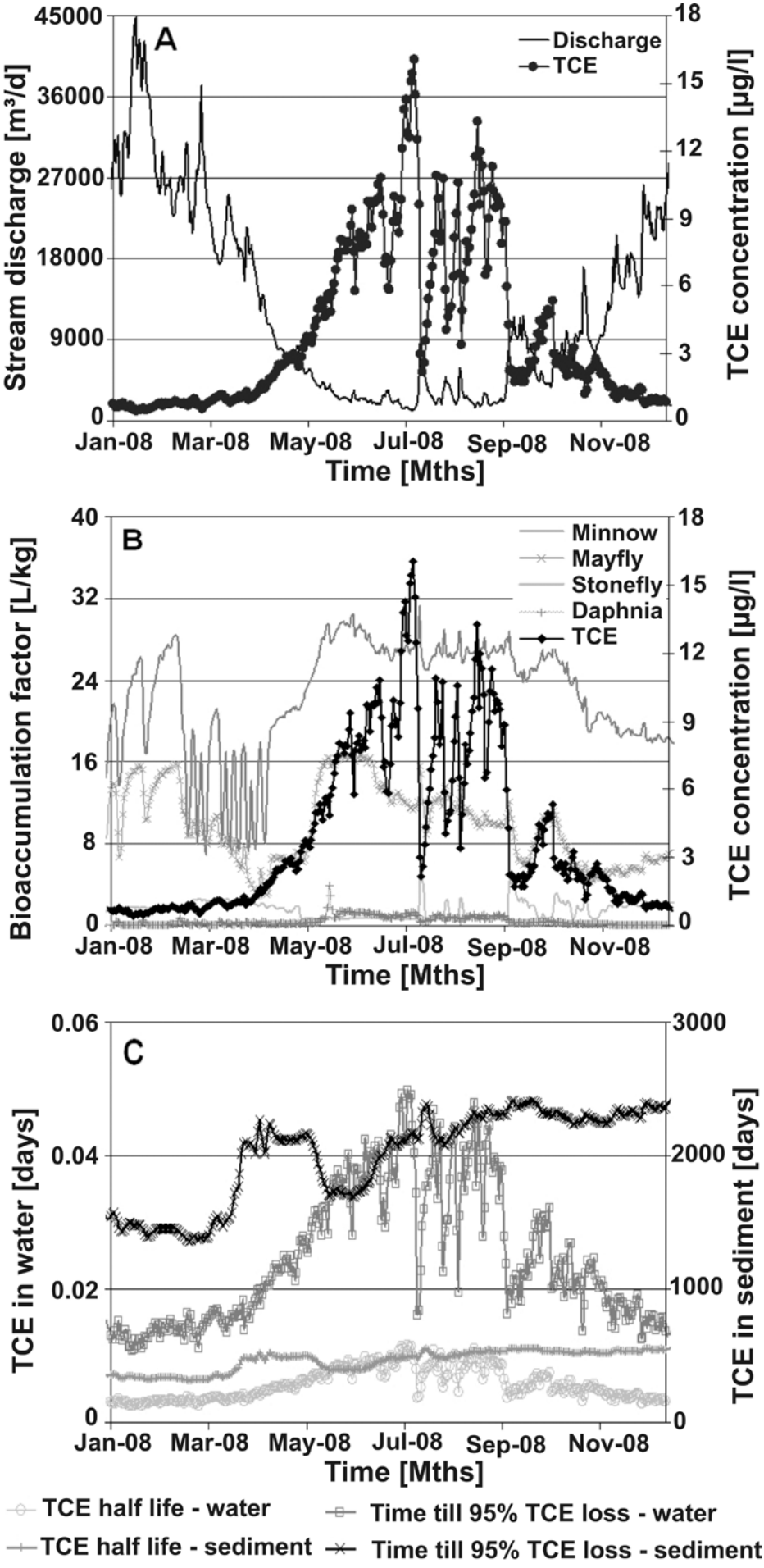
A
Discharge
TCE
Stream discharge [m³/d]
TCE concentration [µg/l]
45000
36000
27000
18000
9000
0
18
15
12
9
6
3
0
Jan-08
Mar-08
May-08
Jul-08
Sep-08
Nov-08
Time [Mths]
B
Minnow
Mayfly
Stonefly
Daphnia
TCE
Bioaccumulation factor [L/kg]
TCE concentration [µg/l]
40
32
24
16
8
0
18
15
12
9
6
3
0
Jan-08
Mar-08
May-08
Jul-08
Sep-08
Nov-08
Time [Mths]
C
TCE in water [days]
TCE in sediment [days]
0.06
0.04
0.02
0
3000
2000
1000
0
Jan-08
Mar-08
May-08
Jul-08
Sep-08
Nov-08
Time [Mths]
TCE half life - water
Time till 95% TCE loss - water
TCE half life - sediment
Time till 95% TCE loss - sediment

Figure 7: *AQUATOX* results for (a) stream discharge and (b) bioaccumulation factor vs. TCE concentration for the 300 m groundwater-impacted stream stretch, and (c) half-lives for both TCE in water and sediment, as well as time required for 95% TCE loss in both water and sediment.

Figure 7b illustrates the modeling results for the calculated bioaccumulation factor for four species (*D. magna*, stonefly, mayfly and minnow) versus TCE concentration. A trend clearly exists, with an increasing bioaccumulation factor from the lowest to the highest trophic level (i.e. moving from *D. magna* to minnow and bottom to top in Figure 7b). It can also be seen that the bioaccumulation factor increases with TCE concentration in the summer months (i.e. from May to September).

D. magna was found by *AQUATOX* to be the most sensitive species modeled (data not shown). However, a close comparison of the *D. magna* concentration between the perturbed and control (no TCE present) scenarios indicates that there were no ecosystem effects occurring. This low ecosystem impact is expected as the NOAEC for this organism and TCE is 1,384 μgL^{-1} (U.S. EPA, 2009a), which is much higher than the observed surface water concentration of 17.4 μgL^{-1}.

The half life of a contaminant provides a good indication of the length of time in which a stream will be impacted by the contaminant. Figure 7c depicts the modeled TCE half life in water and sediment (bottom two curves) and the time for 95% chemical loss (upper two curves). Both parameters in water (versus sediment) follow the trend for TCE concentration (depicted in Figure 7b). In contrast, both half life and time for 95% chemical loss in sediment are less affected by the dynamically changing TCE concentration. Simulations were carried out for 5 years (2008-2012), and it was observed that the trends evident in Figure 7 simply repeat themselves, producing a yearly cycling pattern (data not shown).

4.7 Uncertainty assessment

Monte-Carlo simulation was used to assess the uncertainty of the results from the groundwater transport model, focusing on the role of the highly uncertain or effective parameters on the decision process. Table 7 lists the parameters and ranges applied for the analysis. Input parameters were described using either triangular or uniform distributions, where the degree of variation (i.e. spread) reflected the estimated uncertainty for a specific parameter (e.g. van Groenendaal and Kleijnen, 2002).

TABLE 7

Simulations were done for an ensemble of 500 realizations. The outcome was then screened in order to generate a subset of realizations that are consistent with actual site data. A subset of 112 realizations was produced utilizing a screening criterion that requires the predicted (model) concentrations to be within ±50% of the observed concentration measured at the receptor in 2005.

Uncertainties in input data (Table 7) lead to uncertainties in model output. The simulation results show that TCE concentration and resulting risk to the receptor may be approximately three times higher or two times lower than was predicted for the base case (Figure 8). Interestingly, two “trends” or sets of curves can be distinguished in Figure 8. A deterministic sensitivity analysis using the allowable, i.e. screened parameter ranges showed that lower values of hydraulic conductivity were responsible for the set of curves appearing with a later breakthrough time, i.e. in 2000. Both transverse vertical dispersivity and DNAPL pool length had no observable effect on the time for the first breakthrough, but were instead responsible for the resulting “spread” of both maximum concentration and risk indices. This also plays a role in model predictions in which contaminant concentrations can be expected to decrease as a result of the pump and treat strategy.

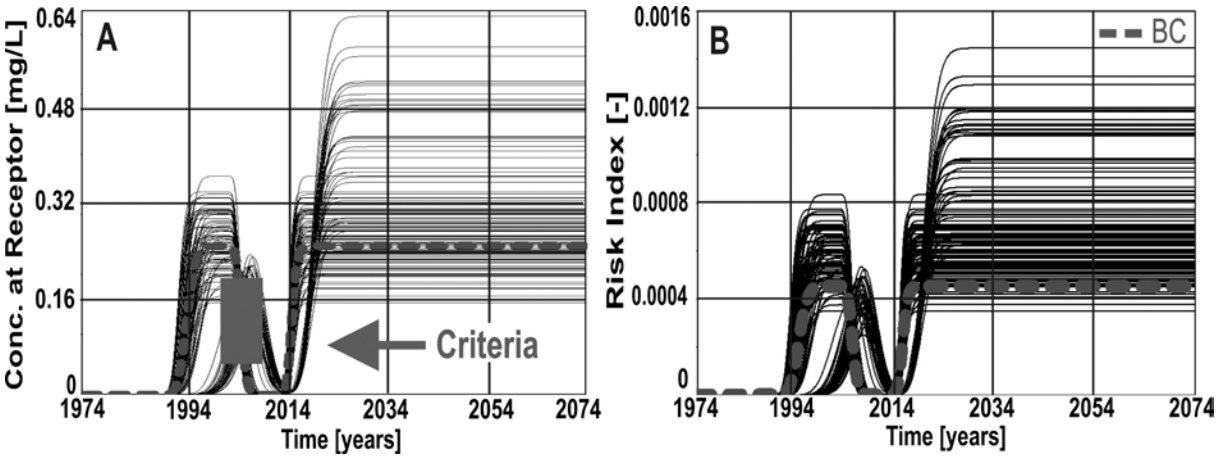

Figure 8: Monte-Carlo realizations of the transport and risk assessment model for (a) concentration at receptor and (b) risk index over time. Note that the base case (BC) model run is indicated in both figures as a dashed line. The model screening criteria (predicted concentrations at receptor = observed concentration at receptor ± 50%) is indicated in (a) by the range allowed (vertical bar) in 2005.

A synopsis of the results of the Monte-Carlo simulation is provided in Table 8. Ranges of input parameters are narrow compared with the previously defined ranges (see Table 7) as a consequence of model screening. The coefficient of variation (CV) may be used to quantify how the original uncertainties have "propagated" through the modeling system. The probability distributions of input and output parameters appear to be very similar.

TABLE 8

The results of the sensitivity analysis for the output variables were also analyzed for the October 2021 (indicated as *t = 10-2021* in Figure 9) time step corresponding to the time of maximum risk value, using histograms. For both concentration at receptor and risk index, the

base case values fell into the ranges containing the largest probability with predicted probabilities of 24% and 22%, respectively.

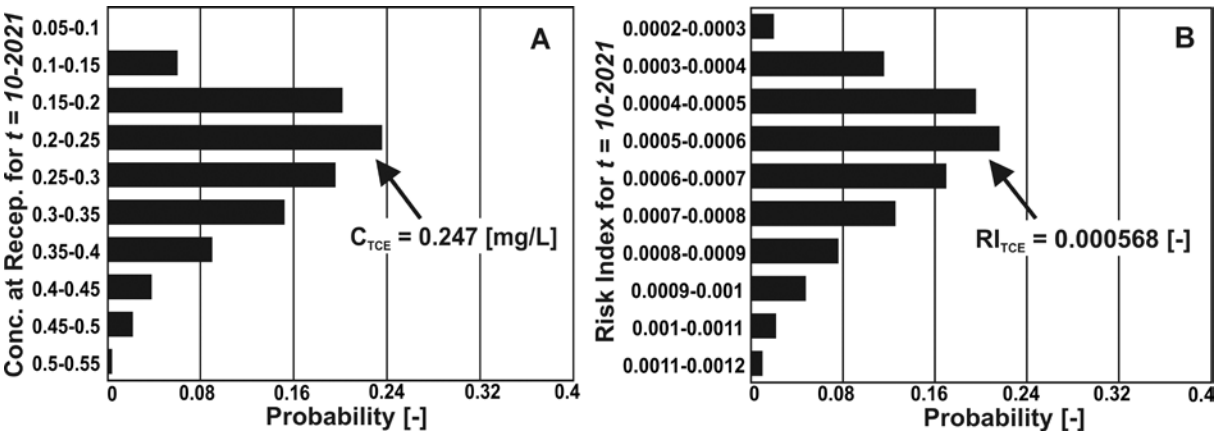

Figure 9: Histograms showing the probability distribution for (a) TCE concentration at receptor and (b) risk index at the expected time of maximum risk (*t = 10-2021*). The specific subset range containing the base case modeled value is indicated by arrows.

5 Conclusions

This paper has shown how integrated modeling can support both human health and ecological risk assessments for surface waters potentially impacted by point sources in groundwater. The decision support system *CARO-PLUS* allows for a model-based, multi-compartmental environmental impact assessment designed to establish the suitability of management scenarios capable of meeting pre-defined, site-specific compliance criteria. It is based on a quantitative exposure assessment and determination of risks for potential receptors deemed relevant for a particular site. This approach is intended to evaluate and reduce the number of competitive options for any further detailed assessment.

The results of the screening tool at the Skensved site indicate an unsettling trend, with TCE concentrations (in groundwater) reaching a maximum of 250 μgL^{-1} that will hold steady for many decades to come. The plume today is under hydraulic control, but the results suggest

that pump and treat, functioning either as a remediation or as a containment strategy, may not be a sustainable management solution for this site.

For the human health risk assessment in surface water, no (carcinogenic) risk was found for the developed worst-case scenario, i.e. children, in a recreational setting. Measured and modeled TCE concentrations in surface water were found to be below the estimated maximum allowable concentrations in water for meeting the risk management target of 10^{-6}. These results are dependent on the actual values chosen for the scenario. Risk was only found to exist if the groundwater was to be used as drinking water, with maximum modeled concentration and risk values of 247 μgL^{-1} and 5.68×10^{-4}, respectively.

The results of the volatilization model could be used to determine the stream reach over which surface water quality criteria has been exceeded. This corresponded to the 300 m stretch where the TCE plume actually infiltrates the Skensved stream. TCE concentrations, as well as water levels were used for a preliminary verification to support the quantitative ecological risk assessment. The applied ecosystem model *AQUATOX* was found to capture these trends well, when compared with actual data. Two major drawbacks, however, were found to exist when using the *AQUATOX* model for preliminary assessment: the extremely large number of parameters needed to create a functioning ecosystem, and the fact that specific organisms not currently included in the model cannot be added by the user.

For the ecological risk assessment, it was found that the TCE contamination does not have any significant effect on the stream ecosystem. These results indicate that volatile organic solvents may not pose a threat to surface water ecosystems. Caution is warranted, however, since the only chemical investigated was TCE and ecosystem effects were modeled based on the impact of TCE on three indicator organisms assumed to represent common species in small Danish streams. This is also reflected in the high NOAEC values found for all organisms investigated. Further modeling studies are needed, including studies comparing ecosystem impacts for both chronic and acute toxicants. We additionally propose that

conducting subsequent supplementary field studies is highly necessary to improve the evaluation of modeling results, when ecosystem modeling input is restricted to only a few species which potentially are not present at the site in question.

Uncertainty with respect to transport modeling parameters was also investigated. The hydraulic conductivity was found to be the most critical site-specific parameter, suggesting that additional effort should be directed towards it when prioritizing future investigation needs. Sensitivity analyses confirmed that an evaluation of uncertainties for site-specific parameters is critical to sound decision-making and must be taken into consideration in any quantitative assessment.

The implementation of system dynamics to hydrogeological issues recognizes the increasing importance of interdisciplinary systems research that relates policy assessment to resource management options. The risk assessment tools developed in this paper serve to integrate multiple issues, interest groups, disciplines and scales in order to address the wide-ranging impacts of controllable and uncontrollable socioeconomic, ecological, hydrological and institutional drivers.

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Tables:

Table 1: Water chemistry and redox parameters measured at Skensved stream (Christensen and Raun, 2005).

Parameter	**Multilevel samplers**	**Seepage meter**	**Skensved stream**
pH [-]	6.7 – 8.1	6.9 – 7.0	7.6
Temperature [ºC]	9.4 – 15.3	10.3 – 13.8	10.7 – 10.8
Chloride [mgL^{-1}]	50 – 278	71 – 104	24 – 26
Oxygen [mgL^{-1}]	0.2 – 3.5	0.3 – 0.5	8.5
Nitrate [$mgNL^{-1}$]	0.4 – 6.4	1.8 – 2.0	1.8 – 1.9
Dissolved Iron [mgL^{-1}]	< 0.3 – 1.2	n.a.	n.a.
Sulphate [$mgSL^{-1}$]	7 – 41	14 – 17	9 – 10

Table 2: General (best estimate) parameter values used in the base case scenario, including aquifer, site and contamination parameters.

Aquifer Parameters	**Estimate**	**Reference**
Thickness [m]	10	GEO (2009)
Hydraulic conductivity [md^{-1}]	19	Calibration parameter; Christensen and Raun (2005)
Hydraulic gradient [-]	0.00473	Christensen and Raun (2005)
Effective porosity [-]	0.02	GEO (2009)
Seepage velocity [md^{-1}]	4.5	Calculated
Site Parameters	**Estimate**	**Reference**
Aquifer material organic carbon content [-]	0.002	Christensen et al. (1996)
Depth to GW [m]	2	GEO (2009)
Longitudinal dispersivity [m]	6.86	Calculated (Xu and Eckstein, 1995)
Transverse vertical dispersivity [m]	0.0001	Klenk and Grathwohl (2002)
Distance from source to P&T well [m]	500	Christensen and Raun (2005)
Distance from source to receptor [m]	750	Christensen and Raun (2005)
Minimum (summer) surface water flux [m^3d^{-1}]	544	Bruun and Rose (2005)
Contamination Parameters	**Estimate**	**Reference**
Pool width [m]	11	Calibration parameter
Pool length [m]	15	Calibration parameter
Thickness [m]	10	Calibration parameter

NAPL molecular weight [$gmol^{-1}$]	131.4	U.S. EPA (2009b)
NAPL density [kgl^{-1}]	1.46	U.S. EPA (2009b)
Interfacial tension NAPL/water [dynes cm^{-1}]	42	Mayer and Hassanizadeh (2005)
Interfacial tension NAPL/air [dynes cm^{-1}]	32	Mayer and Hassanizadeh (2005)

Table 3: Summary of the human health assessment including initial set of exposure pathways and their corresponding maximum $RI_{i,k}$.

Exposure pathways	**Maximum $RI_{i,k}$ [-]**
Drinking water ingestion	**5.65E-04**
Fin fish ingestion	**2.23E-06**
Shoreline sediment ingestion	3.63E-11
Soil ingestion	3.75E-08
Inhalation of re-suspended soil	2.71E-10
Outdoor air inhalation	1.68E-07
Soil dermal contact	6.25E-08
Shoreline sediment dermal contact	1.21E-10
Maximum RI_i [-]	5.68E-04

Table 4: Input parameters for the volatilization model.

Parameter	**Value**	**Reference**
TCE concentration in groundwater [μgL^{-1}]	130	*CARO-PLUS* output
Stream depth [m]	0.11	Minimum value; Bruun and Rose (2005)
Stream width [m]	1.4	Average value; Bruun and Rose (2005)
Surface water flux [md^{-1}]	3366	Bruun and Rose (2005)
Volatilization rate [d^{-1}]	19	Fitting parameter
Groundwater inflow rate I [$Lm^{-2}d^{-1}$]	360	Fitting parameter
Groundwater inflow rate II [$Lm^{-2}d^{-1}$]	30	Fitting parameter
Groundwater inflow rate III [$Lm^{-2}d^{-1}$]	18	Fitting parameter

Table 5: Parameter values used in the assessment of human health (i.e. children) exposure to contaminated surface water.

Parameter	**Value**	**Notes/References**
Exposure frequency, EF [dyr^{-1}]	90	Best estimate, recreational scenario
Exposure time for outdoor activity, ET [hrd^{-1}]	0.75	Best estimate, recreational scenario
Surface water ingestion rate, IR_w [Ld^{-1}]	0.05	U.S. EPA (1997b)
Inhalation rate, IR_a [m^3d^{-1}]	7.5	ECETOC (2001)
Body weight, BW [kg]	21.4	ECETOC (2001)
Averaging time, AT [yr]	75	ECETOC (2001)
Unit conversion factor, CF_1 [$Lmcm^{-1}m^{-3}$]	10	Default; U.S. EPA (1991)
Volatilization factor of Andelman (1990), K [Lm^{-3}]	0.5	Default; U.S. EPA (1991)
Exposure duration, ED [yr]	6	Default; U.S. EPA (1991)
Exposed skin surface area, SA [m^2]	0.9052	Calculated as 423 cm^2/kg; ECETOC (2001)
Skin permeability coefficient, K_p [cm hr^{-1}]	0.0157	Chemical-specific; RAIS (2009)
Fraction of contaminant absorbed in the gastrointestinal tract, GI [-]	1.0	Chemical-specific; RAIS (2009)
Oral slope factor for ingestion pathway, SF_o [kgd mg^{-1}]	0.4	Chemical-specific; RAIS (2009)
Oral slope factor for inhalation pathway,	0.4	Chemical-specific;

SF_i [kgd mg^{-1}]		RAIS (2009)
Oral slope factor for dermal contact pathway, SF_d [kgd mg^{-1}]	0.4	Chemical-specific; Calculated as SF_o/GI (U.S. EPA, 2004)

Table 6: Parameter values used in *AQUATOX* for the assessment of ecological health.

Animal toxicity data	**Initial conditions [g m^{-2} dry]**	**LC50 [µg L^{-1}]**	**LC50 experimental time [h]**	**Lipid fraction [-]**	**Average wet weight [%]**
Stonefly	0.5[c]	70000[a]	48[a]	0.05[c]	0.03[c]
Oligochaete	1[c]	132000[a]	48[a]	0[c]	0[c]
Minnow	2[c]	52000[b]	24[b]	0.047[c]	2[c]
Ostracod	0.65[c]	56000[a]	48[a]	0.05[c]	0.002[c]
Chironomid	0.5[c]	42000[a]	48[a]	0.06[c]	0.0006[c]
D. magna	0.03[c]	22000[c]	24[c]	0.06[c]	0.0006[c]
Plant toxicity data	**Initial conditions [g m^{-2} dry]**	**EC50 photo [ug L^{-1}]**	**EC50 experimental time [h]**	**Lipid fraction [-]**	
Macrophytes	2[c]	0	0	0.02[c]	
Bluegreens	1.2[c]	63000[c]	192[c]	0.05[c]	
Greens	0.05[c]	390000[b]	96[b]	0.05[c]	
Diatoms	1.2[c]	150000[c]	96[c]	0.05[c]	

a) Kegley et al. (2008)

b) Rippen (1995)

c) U.S. EPA (2009a)

d) U.S. EPA (2009c)

Table 7: Site-specific parameters varied in the Monte-Carlo sensitivity test.

(Input) Parameter	**Estimate**	**Min**	**Max**	**Peak**
Hydraulic conductivity [md^{-1}]	19	9.5	28.5	-
Transverse vertical dispersivity [m]	0.0001	0.00004	0.00015	-
DNAPL pool length [m]	15	10	30	15

Table 8: Summary statistics for the Monte-Carlo simulations for selected input and output parameters (at *t = 10-2021*).

Parameter	**Min**	**Max**	**Median**	**Mean**	**StDev**	**CV**
Input parameters						
Hydraulic conductivity [md^{-1}]	10.96	20.69	18.26	16.64	3.46	0.21
Transverse vertical dispersivity [m]	4.0E-05	1.5E-04	9.0E-05	9.3E-05	3.2E-05	0.35
DNAPL pool length [m]	10.95	29.41	17.04	17.89	4.43	0.25
Output parameters						
Concentration at receptor [mgL^{-1}]	0.153	0.489	0.273	0.279	0.065	0.23
RI [-]	3.52E-04	1.12E-03	6.26E-04	6.41E-04	1.49E-04	0.23